CHAPTER 4

ECOLOGICAL RISK

Introduction

Following the work and recommendations of the National Academy of Sciences panel (NRC, 1983), US EPA created a Risk Assessment Forum to formulate and prepare the agency's guidelines for ecological risk assessment. Improved risk assessment and management have been a major goal of the EPA's ORD research. Risk assessment is the basis for both policy and technical decisions to determine priorities for management and to guide the actual process of managing ecological and other risks.

The EPA's Advisory Committee (US EPA, 1990) identified four broad categories of risks: (1) human cancer risk, (2) human non-cancer risk, (3) ecological risk, and (4) welfare risk. This chapter focuses on aquatic ecological risk.

In 1992 the Risk Assessment Forum (US EPA, 1992a) published its *Framework for Ecological Risk Assessment* that explained the ecological risk assessment paradigm. The 1992 Framework report was followed by several developmental documents. The US EPA (1994a) document presented position papers and their peer reviews on eight important topics related to the ecological risk assessment. The US EPA (1996) report then presented a draft outline of the risk assessment methodology. Definition and application of ecological risk assessment is contained in the first forum report (US EPA, 1992a) :

> *Ecological risk assessment is defined as a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors. A risk does not exist unless (1) the stressor has an inherent ability to cause one or more adverse effects and (2) it co-occurs with or contacts an ecological component (i.e., organisms, population, communities, or ecosystem) long enough and at a sufficient intensity to elicit the identified adverse effect. Ecological risk assessment may evaluate one or many stressors and ecological component.*

Ecological risks can be expressed as probabilistic estimates of both the adverse effects and exposure elements, or as deterministic or even qualitative. The generic risk assessment methodology outlined in the US EPA (1992a) document has the following steps (Figure 4.1):

(1) Problem formulation:

- define stressor characteristics and ecosystem potentially at risk and ecosystem effects,
- endpoint selection,
- the conceptual model,
- analysis plan;

(2) Analysis:

- characterization of exposure to stressors,
- characterization of the relationship between stressor levels and duration of exposure and ecological effects;

(3) Risk characterization:

- risk estimation, including uncertainty,
- risk description,
- risk communication (intercommunication with the stressor managers).

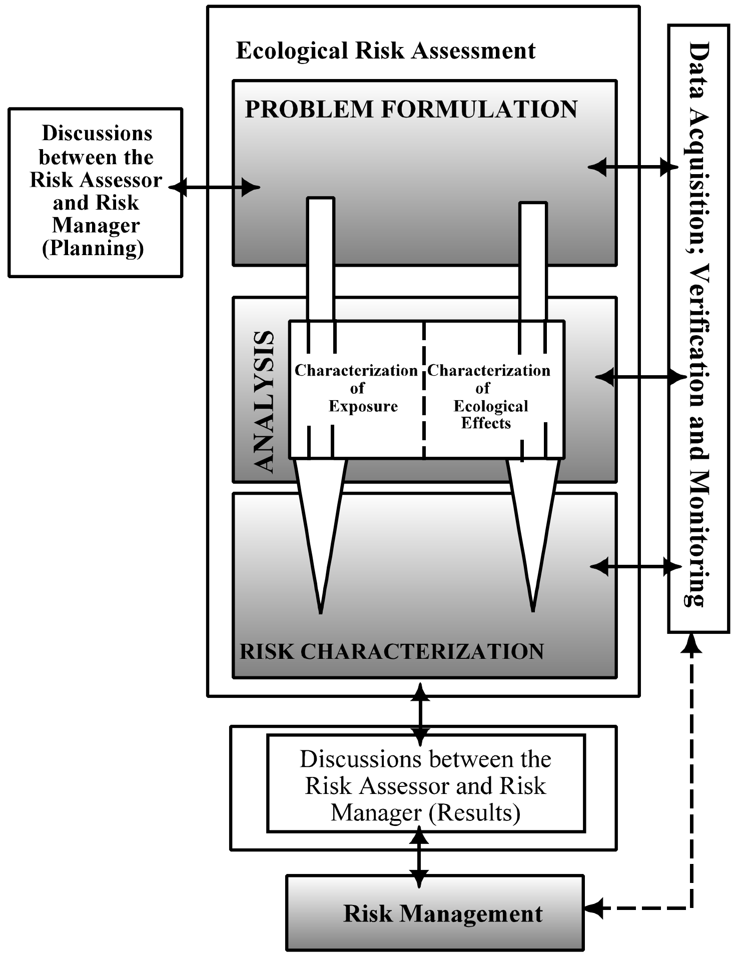

Figure 4.1. Concept of Ecological Risk Assessment (US EPA, 1992a, 1996)

Assessment end points are "explicit expressions of the actual environmental value that is to be protected". These assessment end points must be ecologically relevant to the ecosystem they represent and susceptible to the stressors of concern.

Conceptual models link anthropogenic activities with stressors and evaluate interrelationships between exposure pathways, ecological effects, and receptors. The stressor-response profile may evaluate single species, population, general trophic levels, communities, ecosystems, or landscapes. If a single species is affected, effects should represent appropriate parameters such as effects on mortality (acute toxicity), growth, and reproduction, (chronic effects), while at the community level, effects can be summarized in terms of structure or function depending on the assessment endpoint. The stressor-response profile summarizes the nature and intensity of effect(s), the time scale for recovery (where appropriate), causal information linking the stressor with observed effects, and uncertainties associated with the analysis. The US EPA (1996) guidelines suggest that risks can be estimated by integrating exposure and stressor-response profiles using a wide range of techniques such as comparison of point estimates or distributions of exposure and effects data, process models, or empirical approaches such as observation of field data.

The risk assessment process requires data for developing the model, the stressor distribution and probabilities and interrelationship between the stressor and endpoint effect. Data are also needed for verification of the model. The data could be a part of ongoing routine monitoring (for example, water quality or effluent monitoring collected in special surveys, e.g., a survey of indigenous species that are affected). Monitoring can provide input to all phases of the risk assessment process. For example, monitoring can provide the impetus for initiating a risk assessment by identifying changes in ecological conditions. In addition, monitoring data can be used to evaluate the results predicted by the risk assessment (US EPA, 1996).

US EPA has recognized ecological risk assessment as important for environmental decision making because of the high cost of eliminating environmental risks associated with human activities and the necessity of making regulatory decisions in the face of uncertainty. Ecological risk assessment are frequently conducted in tiers that proceed from simple evaluations of exposure to more complex assessment.

Risk communication is an important part of risk assessment. While the EPA risk assessment framework forum reports and guidelines specify "risk managers" as the recipients of the information, the Marquette University research team added and investigated the attention citizens paid to news about flood risk and news about risk to the ecological health of the river.

The concept of ecological risk assessment and its application has also been developing in the European Community as exemplified by the European Community Directive 93/67/EEC that outlined the principles of the assessment of risks to man and the environment. The risk assessment procedure is almost identical to that proposed by the US EPA, i.e., (1) hazard identification, (2) dose-response assessment, (3) exposure assessment and (4) risk characterization.

Selection and Development of Ecological Risk Assessment Methodology

The proposed USEPA (1996) guidelines give a lot of freedom to the risk assessors to select the methodology. This may be justified as some may claim that many cases are unique and may require individual approaches. However, when the ecological integrity of a water body is considered the selection of the methodology is constricted by the Water Quality Standards Regulations (40 CFR 131, US EPA, 1994b) and by the Clean Water Act itself. Therefore, the term "selection" of the methodology is more appropriate than the term "development".

Selecting Assessment Endpoints

Figure 2.6 in Chapter 2 has shown the block diagrams of causes, stressors and endpoints of the ecological risk as derived from the preambles of the Clean Water Act. The goal of the Clean Water Act in Section 101(a) is *... to restore, maintain the chemical, physical, and biological integrity of the nation's waters.* Therefore, integrity of the water body is the end point if ecology is considered. In ecological interpretation, the integrity of a water body implies an ability of its ecological system to support and maintain a balanced, integrated, adaptive community of organisms having a species composition, diversity and functional organisms comparable to that of natural biota of the region (Karr and Dudley, 1981). The physical integrity implies habitat conditions of the water body that would support the balanced biological community. Chemical integrity would mean a chemical composition of water and sediments that would not be injurious to the aquatic biota. A composition of aquatic organisms resembling or approaching that of unimpacted similar water bodies in the same ecoregion without invasive species represents the biological integrity.

Figure 2.6 depicted the hierarchical concept of integrity. In the figure a notion of a *supreme endpoint* became evident. The chemical and physical end points are inputs in the model to the biotic integrity that, in the aquatic ecology concept, is the supreme endpoint (Karr and Chu, 1999). A somewhat different interrelationship may be developed if human health is the supreme endpoint; however, a healthy aquatic biota is also necessary prerequisite for a safe water supply, fish consumption and contact recreation that affect human health.

The effects of contaminants on living organisms are generally evaluated using the basic concepts that were originally formulated by Sprague (1969):

Acute toxicity. The exposure of organisms to a compound or a mixture of compounds will result in a crisis, usually short in time during or following the exposure.

Chronic toxicity. The exposure will have a sublethal damaging impact on the organisms occurring over a longer period of time up to the entire life cycle.

Lethal toxicity. Exposure will result in death of organism.

Sublethal toxicity. Exposure is damaging to the organism, but it will not result in death.

Cumulative toxicity. The effects on the organisms are brought about, or increase in strength, by successive exposure

Methodology

This chapter describes methodology of evaluating chemical risk from water quality and sediment, respectively. The methodology has been applied to two watersheds located in southeastern Wisconsin: Oak Creek and Menomonee River. The Oak Creek watershed is still rural but rapidly developing while the Menomonee River watershed has been already developed with the exception of its upstream areas.

Traditional approaches to evaluating water quality compare measured values to a set of criteria, specified either by a regulatory agency or by its effect on organisms. Alternatively, the ecological impact of pollutants in receiving waters can be evaluated using the risk assessment process. Traditional water quality evaluation can be found in Report #7 (Bartošová et al., 2000). Toxicity has been evaluated using the risk assessment approach.

Acute toxicity criteria are determined for the one-hour average concentration, not to be exceeded more than once in three years on an average. *Chronic toxicity criteria* are specified for the four-day average concentration, not to be exceeded more than once in three years on an average. Since most of the water quality constituent concentrations follow a log-normal distribution, the acute toxicity criterion corresponds to the 99.9 percentile log-cumulative probability characteristics of maximum daily concentration. Similarly, the chronic toxicity criterion would be violated if 99.5 percentile of average daily concentrations exceeded the criterion.

The more accurate (and conceptually cleaner) procedure, as outlined in the WERF methodology by Parkhurst et al. (1996) and modified for stormwater discharges by Novotny and Witte (1997), removes the consideration of the water quality criteria completely. Instead, the methodology is based on a direct consideration of the joint probability of two probability functions: (1) the probability density function of the event mean concentrations (EMC) adjusted for the appropriate dilution ratio (DR) and water effect ratio (WER) effects, f(EMC) = pdf(EMC x DR/WER), and (2) the risk function g(R|EMC), which gives the value of the probability that an organism will be adversely affected by the exposure to the given stormwater EMC (as modified by DR and WER), and considering also the effects of water hardness on the LC_{50} values.

In-Stream Water Quality

Overview of Modified WERF Methodology

Novotny and Witte (1997) provided the extension of the WERF risk characterization methodology that was outlined previously by Parkhurst et al. (1996). This extension is designed to allow the application of the methodology to estimating the toxicological-ecological impacts of *stormwater*. The ecological impacts of stormwater include the degradation of aquatic habitat by flow, as well as the toxicological-ecological impacts on water quality. The overall ecological state of the receiving water body can be ascertained using a biological evaluation, such as that outlined in the *Rapid Bioassessment Protocol* methodology (Plafkin et al., 1989, Barbour et al., 1997). However, biological assessment procedures of this type are based on the application of multiple indices calling for subjective judgment. The toxicological-ecological component of the overall ecological risk assessment lends itself more readily to numerical expression.

Tier 1: Screening Level

In the screening-level approach, the probability of injury to the indigenous biota from concentration exceeding the criterion value is multiplied by the exceedance probability of the criterion by the concentration in the receiving water body. The corresponding joint probability function can be approximated as follows:

$$p = p_1 p_2 p_{ww} \alpha \qquad \textbf{(4.1)}$$

where p is the overall joint probability of adverse toxicological-ecological effect, p_1 is the safety factor incorporated in the numeric criteria from the 96-hour bioassays using the US EPA procedure (this factor has a value of about 0.001), p_2 is the probability of exceedance of the water quality criterion (which should consider the biological availability effects as expressed in the water effect ratio, WER), p_{ww} is the probability of wet-weather flow (for the Central United States, this probability is about 0.065) or dry weather flow, and α is a factor that considers the effect of the difference between the 96-hour duration of the test exposure and the expected duration of storm events (for an average storm of 9-hour duration, α = 0.3). If wet and dry weather flows are not separated then p_{ww} = 1.0.

Although the application of Eq. 4.1 does remove some of the excess of the conservative nature of a naive application of the water quality criteria, it still overestimates the toxicological risk by orders of magnitude. This can be shown by the application of the more accurate, tier-2 level assessment procedure, which is outlined next.

Tier 2: Risk Quantification for Stormwater Discharges

The more accurate (and conceptually cleaner) tier-2 procedure, as outlined in the WERF methodology by Parkhurst et al. (1996) and modified for stormwater discharges as outlined by Novotny and Witte (1997), removes the consideration of the water quality criteria completely. Instead, it is based on a direct consideration of the joint probability of two probability functions: (1) the probability density function of the event mean concentrations (EMC) adjusted for the appropriate dilution ratio (DR) and WER effects, f(EMC) = pdf(EMC x DR/WER), and (2) the risk function g(R|EMC), which gives the value of the probability that an organism will be adversely affected by the exposure to the given stormwater EMC (as modified by DR and WER), and considering also the effects of water hardness on the LC_{50} values. The joint probability, again taking into account the probability of wet-weather events, is

$$h(R,C) = p_{ww} \mathrm{f(EMC)\ g(R|EMC)} \tag{4.2}$$

Put in words, the joint probability function of Eq. 4.2 gives the probability that (1) a wet-weather event will occur, (2) a particular EMC will occur in the stormwater (given that there is a wet-weather event), and (3) an indigenous organism will be adversely impacted (given that there is a wet-weather event and given that the adjusted EMC is equal to that particular value). The integration of Eq.4.2 over all concentrations, as summarized in Figure 4.2, will then yield the total risk that the stormwater discharges will be adverse to the indigenous aquatic life, *r*.

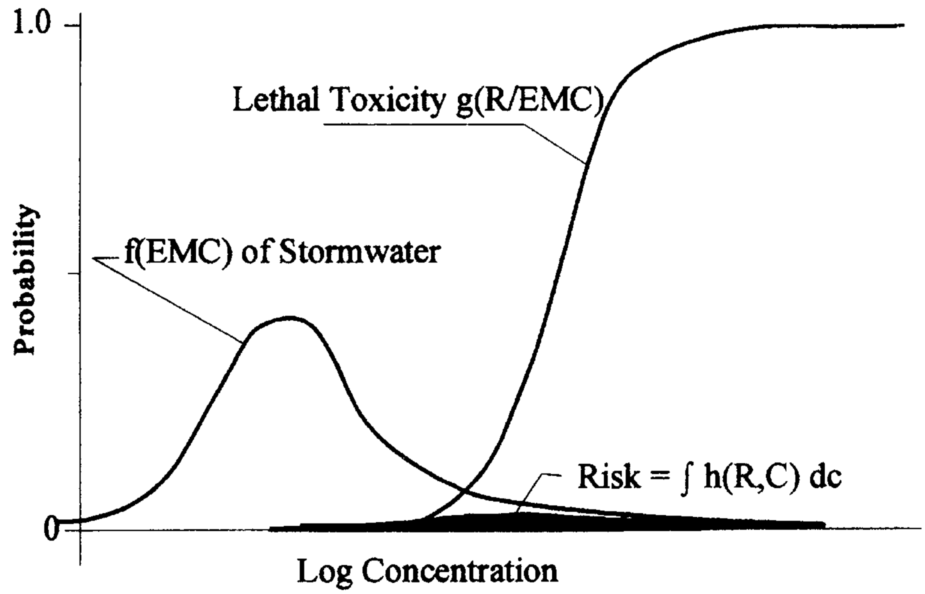

Figure 4.2. Tier-2 ecological risk assessment for stormwater impacts (from Novotny and Witte, 1997).

The *r* value, however, expresses the total risk due to one stressor only. Therefore, the total risk due to all the relevant stressors will be

$$R = \sum r_i \tag{4.3}$$

The stressors may exert a combined effect on an organism (additive), they may interfere one with another (antagonism), or their overall effect may be greater than when acting alone (synergism) (Mason, 1991). An example of an additive interaction is the combined toxicity of zinc and cadmium to fish, though their toxicity is synergistic to algae. Calcium (hardness) is antagonistic to heavy metals.

Statistical Specifications

Given that there are more than 700 species of fish in North America (Suter, 1993) and hundreds of thousands of other aquatic species, the expectation that the limited set of species that have been tested contains the most sensitive species would be quite naive. This assumption is avoided by assuming that the sensitivity of species follows some probability distribution.

Selecting Distribution for Risk Function

The choice of distribution can have a profound effect on the final risk estimation, especially in the area of lower concentrations. There are two distributions involved in risk calculation: (1) distribution of concentration and (2) distribution of toxic response to given concentration. Usually, the distribution of ambient concentration is well described. It has been established by numerous studies that ambient concentration of most parameters follows log-normal distribution. Mean and standard deviation of log-concentrations provide sufficient information to fit the distribution, provided that sample size is large enough. On the other hand, the toxic response curve is defined rather poorly. Depending on specific chemical tested, sometimes only as few as 10 data points are available.

Parkhurst et al. (1996) recommended a linearization of S-shaped curve of LC_{50}s by logit transformation to fit the toxic response curve. Other distributions have been examined and compared, such as a normal distribution, a 3-parametric normal distribution, a Gumbel distribution, or General Extreme Value (GEV) distribution (all in logarithmic space; i.e., the normal distribution is, in fact, log-normal). In addition, Novotny & Witte's linear approximation of lower-tail area (Novotny and Witte, 1997) has been examined.

The following example illustrates how the choice of distribution for toxic response curve effects the value of risk to aquatic biota. The probability distributions have been tested using the LC_{50} values for three metals: copper, zinc, and lead. The normal, Gumbel, GEV and 3-parametric normal distributions were fitted using the method of moments. The coefficients of linear approximation and of logit transformation were estimated by least square method (linear regression). Only results for copper are provided in this report. Bartošová (2000) contains details and information on other metals.

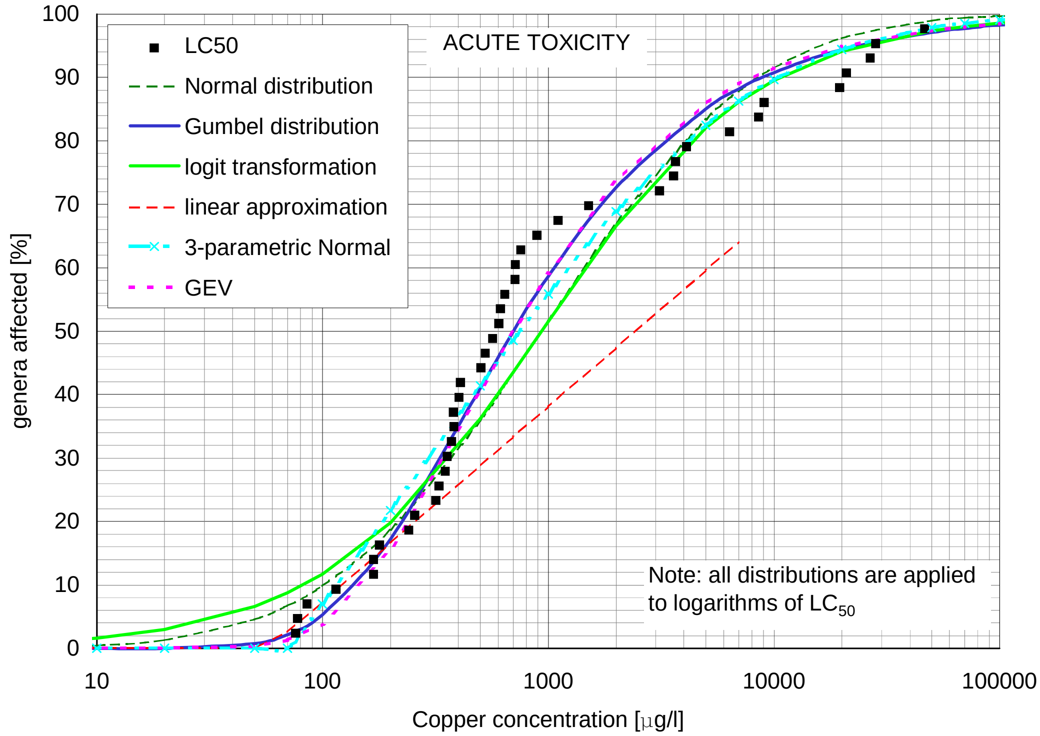

Figure 4.3. Toxic response curve for copper. Comparison of fits for different distributions. Hardness 250 mg $CaCO_3$/l.

Figure 4.3 shows the fits of toxic response curve for copper for several distributions. All distributions investigated generally follow the data and can be used to estimate the empirical distribution of copper LC_{50}. The region of most interest in ecological risk assessment is the lower part of toxic response curve. This is where most of the ambient concentrations are, not in the middle or at higher concentrations. Careful examination of Figure 4.3 reveals that the normal distribution as well as the logit transformation do not capture the behavior of empirical data for LC_{50} in areas of low concentration. Gumbel distribution describes this area much better. This can be also seen from Table 4.1.

Table 4.1. Goodness of fit for tested distributions: copper.

MODEL	Total		First 10 values	
	SSE	**R2**	**SSE**	**R2**
Normal	2,642	0.921	91	0.994
3-parametric normal	1,376	0.959	250	0.983
Gumbel	1,052	0.968	70	0.995
Logit (WERF)	2,553	0.924	191	0.987
Linear (Witte)	10,723	0.679	16	0.999
GEV	1,166	0.965	79	0.994
Total error	33,372		14,292	

Table 4.2 shows the ecological risk calculated for different distributions fitting the toxic response curve. The ambient concentration of copper at site RI-23 follows log-normal distribution with mean of 0.309 and standard deviation of 0.358. This corresponds to the average concentration of 2.04 μg Cu/l. The average concentration of lead and zinc is given in Table 4.2. The average water hardness of 444 mg $CaCO_3$/l was assumed.

Table 4.2. Comparison of acute ecological risks at site RI-23 calculated for different distributions.

Distribution	**Copper**	**Lead**	**Zinc**
mean dissolved concentration [μg/l]	*2.04*	*1.24*[1)]	*4.72*
Normal	2.5 E-04	2.9 E-05	3.1 E-06
3-parametric normal	9.9 E-09	9.2 E-02	7.5 E-03
Gumbel	1.9 E-07	5.1 E-09	1.3 E-09
logit transformation	3.1 E-03	2.4 E-03	2.9 E-04
linear approximation	2.6 E-08	7.9 E-09	3.8 E-07
GEV	5.4 E-08	5.3 E-04	2.8 E-05

1) period after 1987

This example illustrates how the selection of a theoretical distribution can introduce a difference of 4-5 orders of magnitude into the risk calculation. Using logit transformation as recommended by WERF results in relatively high value of risk to aquatic biota. The difference becomes less significant when ambient concentration increases and the integration range comes closer to the range covered by toxicity values (GMAV) where fitted distributions do not differ as much as in low concentration area.

The linear approximation approach differs from the traditional distribution fit approach in that it assumes the existence of some minimal concentration C_{min} below which there is no risk to aquatic biota. This assumption is also employed in the 3-parametric normal distribution. The minimal copper concentration for the above mentioned example is C_{min} = 57.7 μg/l for linear approximation and C_{min} = 70.5 μg/l for the 3-parametric normal distribution. Theoretical probabilistic distributions approach minus infinity on logarithmic scale as the percentage of genera affected approaches zero, i.e. the minimal concentration is C_{min} = 0.0 μg/l. Using the unbounded distributions is more conservative than the assumption of no minimal concentration.

The question is whether the minimal concentration exists. The values defining the toxic response curve are based on LC_{50}s and represent the genera mean acute values (GMAV). The probabilistic approach is based on the assumption that all GMAVs come from the same distribution regardless the genera. Imposing the minimal concentration on distribution would mean that we *know* there is no genus that would exhibit 50% mortality rate below this limiting concentration. However, there is a minimal concentration for every organism, species, or genus. This would correspond to *no observed effect concentration* (NOEC) as detected during chronic toxicity tests. Thus, the minimum concentration has the probability distribution of its own rather than being a single value.

Up to now, only a limited number of species has been tested for toxic response. This makes the task of distribution fitting extremely difficult. There is 42 observations of GMAVs for copper, 35 for zinc, and 10 for lead. The lower the number of observations, the wider the confidence limits for parameter estimation. The Gumbel distribution has been recommended to fit the toxic response curve for copper in ecological risk calculation. The normal distribution has been recommended to fit the toxic response for zinc and lead. The most difficult problem encountered in selecting proper distribution is the lack of information on effects in the area of existing ambient concentrations.

Effect of Hardness

The toxicity relationship for metals were determined from the laboratory tests with standard water hardness of 50 mg $CaCO_3$/l. LC_{50} values are corrected for other values of hardness using the formula provided in the criteria document (US EPA, 1992b):

$$\chi = \frac{LC_{50}(H)}{LC_{50}(50\text{mg / l})} = \left(\frac{H}{50}\right)^{\alpha} \quad \textbf{(4.4)}$$

where H is the hardness [mg $CaCO_3$/l], and α is the parameter specific for given toxic pollutant. For example, for copper α = 0.9422. The risk function thus becomes a family of individual functions defined by distribution of hardness. The risk function integrated over both hardness and heavy metal concentration will yield the total risk that incorporates the effect of hardness.

Two approaches were taken to investigate the effect of hardness on resulting risk: (1) Monte Carlo simulation; and (2) direct integration over two variables. During the Monte Carlo simulation, the variable space was sampled for hardness 5,000 times. For each sampling, the risk function was first adjusted for selected hardness and then integrated over copper concentration. This approach allows us to investigate the distribution of the risk as it changes with hardness. The second approach results in one value of the risk. The direct integration over hardness compacts the family of risk functions into one risk function that already includes the probability distribution of hardness. Further analysis will help to determine what percentile from hardness distribution should be selected for simple evaluation (integration only over the metal concentration).

The following hardness distributions were considered in this analysis (all with normal distribution): mean 300 mg $CaCO_3$/l (st. dev. of 10, 25, 50, 75, and 99), mean 150 mg $CaCO_3$/l (st. dev. of 5, 10, 25, 35, 49), and mean 60 mg $CaCO_3$/l (st. dev. of 5, 10, 15 and 19). The representative (recommended) hardness percentile for all scenarios is shown in Figure 4.4. The recommended percentile in all scenarios varies from 44% to 60% and is decreasing with increasing standard deviation. When standard deviation is normalized by average hardness, the percentiles for all scenarios follow the same function (Figure4.5).

The similar series of calculation was carried out for the normal distribution (zinc and lead). The relationship between recommended hardness percentile and normalized standard deviation is shown in Figure 4.6. The relationships are very similar, regardless of original distribution used to fit the risk function or heavy metal (copper, lead, or zinc). The average hardness has been recommended for adjusting toxic response function of heavy metals.

Calculations of risk in the previous chapter were carried out in Excel. Individual spreadsheets have been established for each investigated metal. Custom developed macros are used to fit selected distributions to a toxic response curve as well as to calculate the risk to aquatic biota for specified water quality site. The software is described in Bartošová (2000).

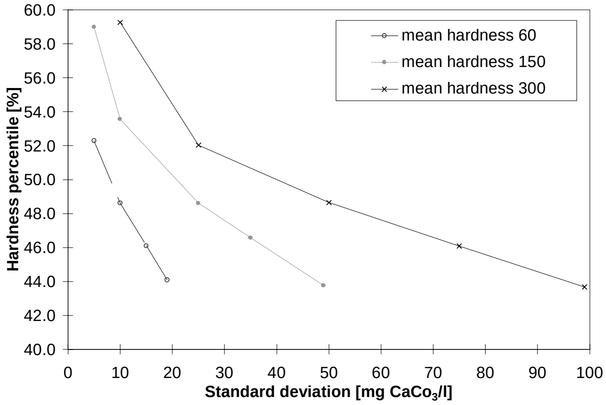

Figure 4.4. Relationship between recommended hardness and hardness distribution (mean and standard deviation). Copper.

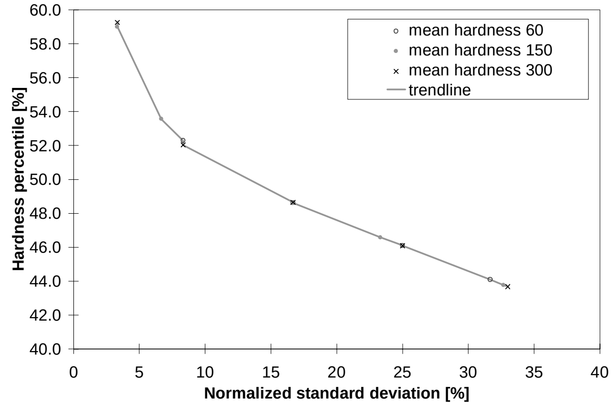

Figure 4.5. Relationship between recommended hardness percentile and hardness distribution (mean and standard deviation). Standard deviation is normalized by mean hardness. Copper.

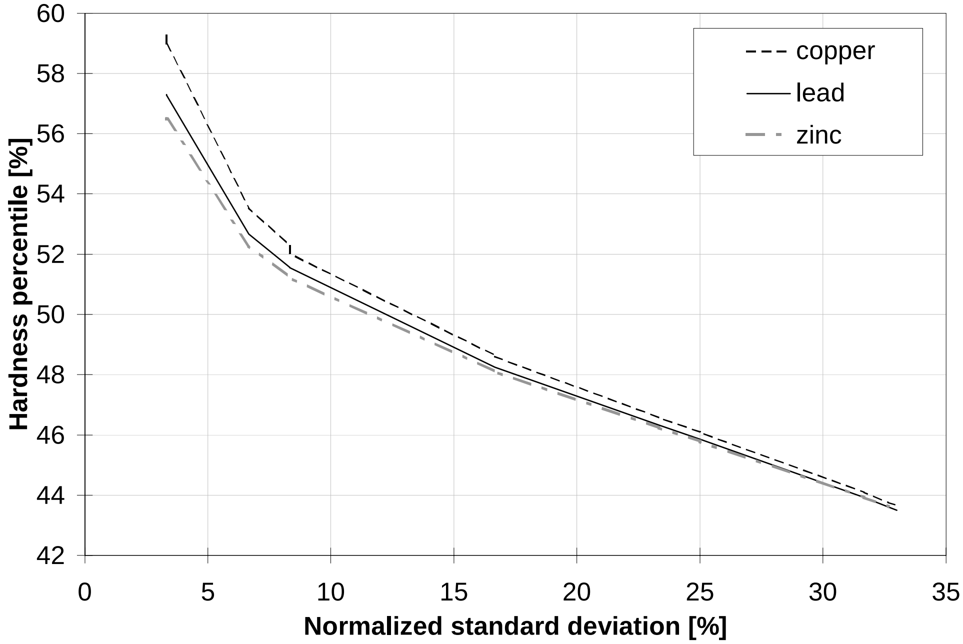

Figure 4.6. Relationship between recommended hardness percentile and hardness distribution (mean and standard deviation). Standard deviation is normalized by mean hardness. Copper, lead, zinc.

Sediment Quality

The above-described methodology was developed for estimating the effects (both acute and chronic) on aquatic biota due to contamination of water column. It does not incorporate the chronic effects of contaminated sediment. This methodology has been modified to enable estimation of ecological risk due to sediment contamination. The major assumptions made in this modification for sediments are: (1) the exposure of receptor organisms is limited to benthic species, and (2) the major and thus only considered exposure route is through the interstitial pore water. Applied to sediments, the joint probability function gives the probability that (1) a particular concentration will occur as a result of partitioning in sediment and (2) an indigenous benthic organism will be adversely impacted by a given concentration of a contaminant.

The sediment data was used to calculate the interstitial porewater concentration for the heavy metals present in the sediment. The constant ratio between the sediment concentration and the interstitial pore water concentration describing equilibrium partitioning (Equation 4.5) was used to find the interstitial pore water concentration.

$$K_p = \frac{C_s}{C_d} \tag{4.5}$$

There are two major obstacles that complicate the use of ecological risk methodology for estimating the effects of contaminated sediment. First, data on sediment quality are often limited. This is especially true for data available from USGS or STORET. Sediment is sampled only once so the distribution of concentration, both spatial and temporal, is unknown. Second, the exact value for the partition coefficient used to estimate pore water concentration from sediment contamination is unknown. These problems have been overcome by assuming variation in partitioning coefficient within the published values. The distribution of partition coefficient thus supplies the needed variation in interstitial pore water concentration. This decision was made after assessing other available partitioning models that required more complete sampling and data of other sediment and water quality characteristics.

Minimum and maximum partition coefficients (Ambrose, 1999) were used to give a maximum and minimum interstitial pore water concentration of the investigated metal. Thus, the calculated interstitial pore water concentrations represent a probable concentration range based on a range of the partition coefficients. Two methods of calculation were compared. In the first method, log normal distribution of concentration defined by the maximum and minimum concentrations was assumed. In this method, the variation is due to the uncertainty of the partition coefficients and does not include inherent uncertainties in the distributions of the sediment samples themselves. The second method is a simplified integration for limited samples. Instead of estimating the distribution of porewater concentration, the probability function f(EMC) takes on two values: one for concentrations less than or equal to the measured concentration C_{MAX}, and zero for concentrations greater than C_{MAX}. The risk calculation is thus simplified to integrating the risk function g(R|EMC) from $-\infty$ to C_{MAX}. The reader is referred to Kasun (2001) for details.

Evaluation of Future Loads using GIS

The sediment and pollutant load to the river system is directly related to land use and human activities on the watershed. Present loads and risks can be evaluated from actual measurements of water and/or sediment quality. Loads generated in the future can be only estimated based on modeling of future scenarios. Geographical information system (GIS) facilitates data input and can also be used for modeling.

ArcView GIS has been used to develop a model of nonpoint pollution from urban and rural land uses. The load from urban areas has been estimated using the SCS method combined with event mean concentrations for pollutants of concern. The load from rural areas has been estimated from erosion and concentration of pollutants in soil. Two approaches have been considered: (1) evaluation of annual load, and (2) event-based evaluation.

The universal soil loss equation (USLE) has been implemented in Arc-View GIS to calculate an estimate of average soil loss: where A is the soil loss in tonnes/hectare for a given storm, R is the rainfall energy factor,

$$A = (R)(K)(LS)(C)(P) \tag{4.6}$$

K is the soil erodibility factor, LS is the slope-length factor, C is the vegetative cover factor, and P is the erosion-control practice factor. Rainfall, land use, soil type, and topographical data were obtained to determine the proper factors for the USLE. The details on obtaining individual factors are described in Technical Report #12 (Blonn and Novotny, 2001).

Unit area loads have been used to estimate annual loadings from urban areas. The sediment loads specific for each present/future land use have been applied to both study watersheds. The load has been calculated as:

$$A_U = \sum_{i \sim landuse} a_i \, l_i \tag{4.7}$$

where a_i is the area of type i land use and l_i is the unit area load for type i land use. Unit area loads for sediment were determined from a study conducted in 1984 as part of the US EPA Nationwide Urban Runoff Program (NURP). Unit area loads for metals were determined based on data measured in a study by PLUARG (Pollution by Land Use Activities-Reference Group of the International Joint Commission). These data were summarized into the form of unit loads by Marsalek (1978).

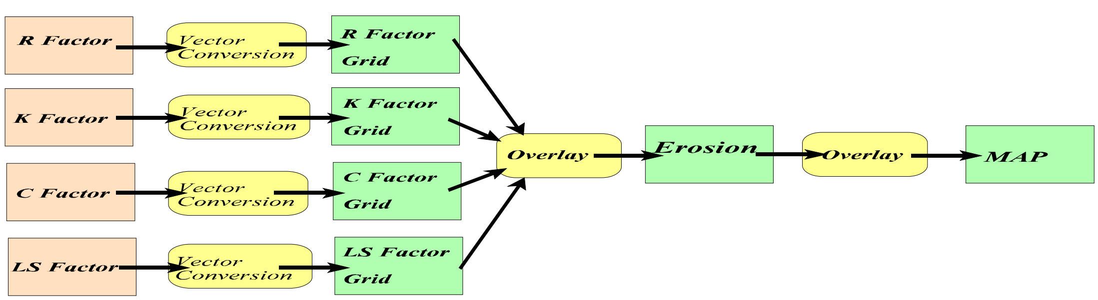

Figure 4.7. Model Builder Diagram for USLE Calculation

Appropriate delivery ratios were applied to the amount of erosion in each watershed based on the land use, impervious area, and degree of storm sewering. As all factors required for calculation vary spatially throughout both watersheds, Arc-View GIS and its extension, Model Builder, were essential in performing the calculations.

The second approach was event based. Data from storms during the period from 1986-1997 have been used for calibration and verification purposes in this study. Rainfall data obtained from the National Weather

Service was analyzed to define the storm events. The rainfall gauge is located at Mitchell International Airport within the Oak Creek watershed.

The urban runoff has been calculated using the SCS method and calibrated against flow measurements. The SCS method is the most widely applied method for estimating the runoff for a rainfall event:

$$Q = \frac{(P - 0.2\,S)^2}{P + 0.8\,S} \tag{4.8}$$

where Q is the urban runoff [mm], P is the precipitation [mm], S = 25400/CN - 254 is the storage constant [mm], and CN is the runoff curve number. The loads have been then calculated for events causing surface runoff ($P > 0.2\,S$) using USLE for rural areas and event mean concentration (EMC) concept for urban areas.

The event based modeling can be particularly useful for assessing changes in probabilistic distribution of pollutants and, consequently, changes in ecological risk due to chemical contamination.

Results and Discussions

Data Description

The methodology described above has been applied to two watersheds in southeastern Wisconsin, the Oak Creek and the Menomonee River watersheds. Water and sediment quality has been monitored by several agencies. GIS data were provided by Southeastern Wisconsin Regional Planning Commission (SEWRPC).

Water Quality Sampling

The EPA water quality retrieval system (STORET) contains water quality data from 6 stations in the Oak Creek watershed as monitored by Wisconsin DNR (WI DNR) and USGS. However, most of these data were measured in 1970s with variable frequency. Milwaukee Metropolitan Sewerage District (MMSD) carries out a separate monitoring program in the Oak Creek watershed. The regular MMSD monitoring program of the Oak Creek watershed started in 1985 and continues until today. Seven stations were sampled regularly during non-winter months (with the exception of 1992 year).

A supplemental monitoring program has been conducted by Water Quality Center of Marquette University as a part of this project. Water column samples and a sediment sample were taken from four sampling sites at Oak Creek during wet weather and dry weather flows. The samples were analyzed for conventional parameters (COD, pH, SS, VSS, TS, total hardness, N-NO_{2+3}, TKN, and TP), total and dissolved heavy metals (Cd, Cu, Pb, and Zn) and PAHs. Cyanides were only analyzed in winter samples.

The Menomonee River watershed has been given greater attention by monitoring agencies than the Oak Creek watershed. The STORET system contains information on 66 stations. However, many of these stations were monitored only for limited time and/or a limited number of parameters were analyzed. There are 11 locations on the Menomonee River, 4 of them in the estuary portion of the stream, and 9 locations on various tributaries such as Little Menomonee River, Underwood Creek, Noyes Creek, Honey Creek and

Schoonmaker Creek. Most of these locations were monitored in 1970's. A separate monitoring program is carried out by MMSD at 9 locations, 4 of them in the river estuary. MMSD stations were sampled regularly once to four times a month during non-winter months from 1980. The program was expanded in 1985 when new stations were added. Not all parameters were analyzed for every sample, though. For example, heavy metal content was not measured at all during 1987-1989 years.

Detail analyses of water quality data is available in Technical Report No. 7 (Bartošová et al., 2000). The ecological risk to aquatic biota was calculated for selected heavy metals. Cadmium was excluded from analysis because of the small number of values measured above the detection limit. It would be impossible to fit the distribution to such data set. The data for copper, lead (both before and after 1987), and zinc were statistically analyzed. A certain proportion of measurements is reported as *data below detection limit*. This does not mean that the concentration is zero, only that it is somewhere between zero and the detection limit. The data follow log-normal distribution. The mean and the standard deviation for those monitoring sites with measurements less than detection limit were estimated from quantile plot, as long as median was above the detection limit. The results are summarized in Tables 4.3 and 4.4. The total concentration reported by MMSD has been transformed to the dissolved concentration using the ratios determined from our monitoring program

Table 4.3. The mean and standard deviation of fitted log-normal distribution for dissolved concentrations [log μg/l]. Oak Creek watershed.

Station ID	Description	Cu	Pb <1987	Pb >1987	Zn
RI-23	Oak Creek at confluence with North Branch	0.309 0.358	1.06 0.449	0.093 0.603	0.674 0.464
RI-24	Oak Creek at Howell Ave.	0.312 0.316	1.07 0.426	0.006 0.602	0.761 0.426
RI-25	Oak Creek at Forest Hill Rd.	0.262 0.344	1.04 0.422	0.016 0.602	0.724 0.403
RI-26	Oak Creek at Nicholson Ave.	0.252 0.374	1.05 0.410	-0.092 0.626	0.686 0.454
RI-27	Oak Creek at 15th Ave.	0.277 0.336	1.06 0.440	-0.053 0.630	0.657 0.460

Table 4.4. The mean and standard deviation of fitted log-normal distribution for dissolved concentrations [log μg/l]. Menomonee River watershed.

Station ID	Description	Cu	Pb <1987	Pb >1987	Zn
RI-16	Menomonee River at County Line Rd.	0.192 0.503	1.03 0.426	-0.031 0.517	0.493 0.424
RI-21	Menomonee River at Butler	0.324 0.473	1.13 0.383	0.041 0.461	0.701 0.462
RI-22	Menomonee River at Hampton Ave.	0.309 0.479	1.10 0.374	0.146 0.510	0.795 0.442
RI-09	Menomonee River at Hart Park	0.263 0.479	0.98 0.409	-0.205 0.458	0.836 0.421
RI-10	Menomonee River at County Stadium	0.267 0.486	1.02 0.368	NA	0.899 0.501

Sediment Sampling

Sediment data were quite limited. The EPA database STORET contains information on 15 sites in the Menomonee River watershed. Wisconsin Department of Natural Resources (DNR) sampled 6 sites on Little Menomonee River, a tributary of Menomonee River, and 6 sites in the Oak Creek watershed. However, information is limited to single sample, i.e., the sampling has not been repeated.

Additional sampling was done by Marquette University Water Quality Center during the course of the project. Sampling included 4 sites in the Oak Creek watershed and 2 sites in the Menomonee River watershed, the subsample of sites selected for water quality and biological monitoring. Tables 4.5 and 4.6 show data on sediment contamination for selected sites in the Oak Creek and Menomonee River watersheds, respectively.

Table 4.5. Summary of sediment data. Oak Creek watershed [mg/kg].

Station ID	Description	Cd	Cu	Pb	Zn
RI-24	Oak Creek at Howell Ave.	NA	105	25	97
RI-26	Oak Creek at Nicholson Ave.	NA	12.2	9.9	14
MU-R	Oak Creek at Ryan Rd.	NA	899	17	251
MU-C	Mitchell Field Drainage Ditch at College Ave.	NA	117	29	100
RI-23	Oak Creek at confluence with North Branch (1997)	1.2	46	48	210

Table 4.6. Summary of sediment data. Menomonee River watershed [mg/kg].

Station ID	Description	Cd	Cu	Pb	Zn
RI-10	Menomonee River at County Stadium	NA	6.54	15	15
RI-22	Menomonee River at Hampton Ave.	NA	2.86	6.9	11
RI-21	Menomonee River at Butler (1989)	2	50	60	250

Literature has been searched for published information on partitioning coefficients. Table 4.7 reports the ranges found for investigated metals (Ambrose et al., 1989).

Table 4.7. Partitioning coefficients for selected metals.

	K_d [l/kg]	
Metals	**Minimum**	**Maximum**
Cadmium	2000	4000000
Copper	6000	1000000
Lead	90000	300000
Zinc	10000	1000000

Water Column Risk

The acute toxicity has been calculated using the methodology described previously. The spreadsheet developed in Excel for risk calculation is described in detail in Technical Memorandum #1 (Bartošová, 2000). The Gumbel distribution has been used to fit the toxic response curve for copper while the normal distribution has been used to fit the toxic response curve for lead and zinc.

The results for Oak Creek watershed are summarized in Table 4.8. The chronic toxicity is approximated by using the Acute-To-Chronic ratio (ACR). This ratio has been estimated for given hardness from EPA water quality criteria. The GMAVs were recalculated using ACR and the values were fitted the selected distributions. The chronic toxicity risk is summarized in Table 4.9. Both acute and toxic risks are in the same order of magnitude for all stations within each parameter. There is an order of magnitude improvement in both acute and chronic toxicity from lead after 1987 year. The chronic toxicity represents a bigger problem than the acute toxicity, especially for lead.

Table 4.8. The acute toxicity risk to aquatic biota. Oak Creek watershed.

Station Number	Cu	Pb <1987	Pb >1987	Zn
RI-23	1.9 E-07	3.0 E-04	2.9 E-05	3.1 E-06
RI-24	7.7 E-08	4.1 E-04	3.2 E-05	4.6 E-06
RI-25	1.6 E-07	3.7 E-04	3.3 E-05	2.7 E-06
RI-26	5.4 E-07	3.6 E-04	2.7 E-05	4.5 E-06
RI-27	1.3 E-07	4.1 E-04	3.1 E-05	4.1 E-06

Table 4.9. The chronic toxicity risk to aquatic biota. Oak Creek watershed.

Station Number	Cu	Pb <1987	Pb >1987	Zn
RI-23	4.7 E-06	1.2 E-02	1.9 E-03	1.7 E-05
RI-24	2.9 E-06	1.6 E-02	2.0 E-03	2.6 E-05
RI-25	4.5 E-06	1.5 E-02	2.1 E-03	1.6 E-05
RI-26	1.1 E-05	1.5 E-02	1.7 E-03	2.4 E-05
RI-27	3.9 E-06	1.6 E-02	1.9 E-03	2.2 E-05

The results for Menomonee River watershed are summarized in Tables 4.10 and 4.11. Similarly to the results for the Oak Creek watershed, both acute and chronic toxicity risks are in the same order of magnitude for all stations within each parameter. The improvement in toxicity from lead after 1987 year reaches two orders of magnitude for acute toxicity and one order of magnitude for chronic toxicity. The acute toxicity from zinc is approximately one order of magnitude lower than the chronic one. The same is true for ecological risk from copper.

Table 4.10. The acute toxicity risk to aquatic biota. Menomonee River watershed.

Station ID	Cu	Pb <1987	Pb >1987	Zn
RI-16	2.1 E-05	4.0 E-04	1.8 E-06	9.9 E-07
RI-21	3.0 E-05	5.0 E-04	1.8 E-06	6.8 E-06
RI-22	3.2 E-05	4.4 E-04	3.5 E-05	8.8 E-06
RI-09	2.3 E-05	3.5 E-04	7.4 E-06	8.7 E-06
RI-10	2.9 E-05	3.5 E-04	NA	3.4 E-05

Table 4.11. The chronic toxicity risk to aquatic biota. Menomonee River watershed.

Station ID	Cu	Pb <1987	Pb >1987	Zn
RI-16	1.6 E-04	1.6 E-02	1.5 E-03	6.2 E-06
RI-21	2.3 E-04	1.9 E-02	1.6 E-03	3.5 E-05
RI-22	2.4 E-04	1.7 E-02	2.5 E-03	4.6 E-05
RI-09	1.8 E-04	1.5 E-02	8.3 E-04	4.6 E-05
RI-10	2.2 E-04	1.5 E-02	NA	1.5 E-05

The risks (both chronic and acute) from copper calculated for the Menomonee River are two orders of magnitude higher than those for the Oak Creek. The risks from lead and zinc are at the same level for both watersheds, with the exception of acute risk from lead after 1987 which is one order of magnitude higher for Oak Creek than for Menomonee River.

Sediment Risk

Lead and copper calculations represented the use of two different risk function distributions: log normal distribution and log Gumbel distribution, respectively. The distribution of the risk function is an important factor in the relationship between the methodologies using log normal distribution of partition coefficients and integrating the risk function to a maximum concentration. For lead, the relationship appears to be linear with a shift determined by hardness (Figure 4.8). When sampling points that account for the same hardness are considered, a nearly perfect linear relationship can be seen between the log normal method and the maximum value method. For copper, the relationship is exponential and there is no apparent deviation similar to that for lead (Figure 4.9).

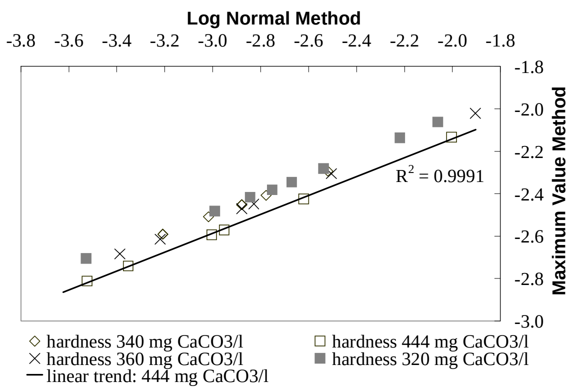

Figure 4.8. Relationship between log normal and maximum value methods for lead

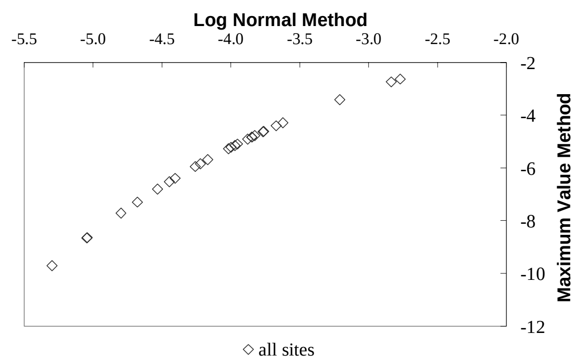

Figure 4.9. Relationship between log normal and maximum value methods for copper

At the lower tail of the risk function distribution the slope of the log normal distribution can be assumed to be nearly constant. This relationship holds true at low interstitial porewater concentrations where the log normal distribution of the risk function holds a nearly constant value. The slope of the Gumbel distribution of the risk function drives the exponential form. The product of the log normal distribution of concentrations from partitioning and the slope of the risk function in the concentration range of the interstitial porewater concentration creates an exponential relationship when compared to the maximum value method.

The log normal distribution of partitioning coefficients was used to calculate the risk to aquatic biota from sediment contamination. The results are shown in Tables 4.12 and 4.13. Values for Cadmium and Zinc are small and represent insignificant risk to the biota. Values for Lead and Copper signify potential concern, especially Copper at site MU-R (Oak Creek at Ryan Road) which had the highest reported concentration (one to two orders of magnitude higher than other sites) .

Table 4.12. The sediment toxicity risk to aquatic biota. Oak Creek watershed.

Station ID	Cd	Cu	Pb	Zn
RI-24		7.5 E-04	7.3 E-04	1.2 E-07
RI-26		2.8 E-06	2.5 E-04	1.2 E-10
MU-R		2.9 E-02	4.7 E-04	1.7 E-06
MU-C		9.4 E-04	8.6 E-04	1.3 E-07
RI-23	4.3 E-07	1.1 E-04	1.5 E-03	1.1 E-06

Table 4.13. The sediment toxicity risk to aquatic biota. Menomonee River watershed.

Station ID	Cd	Cu	Pb	Zn
RI-10		3.0 E-08	4.5 E-04	3.6 E-10
RI-22		5.5 E-07	1.8 E-04	1.2 E-10
RI-21	1.7 E-06	1.7 E-04	2.1 E-03	2.1 E-06

Sediment - Water Quality Interaction

Contamination of the sediment is related to contamination of water column. Surface runoff or point source discharges bring pollutants into receiving waters. There is a continual exchange of pollutants between sediment and water. Thus, one would expect to see correlation between sediment and water column risks. Figures 4.10, 4.11, and 4.12) show the relationship among these risks separately for individual metals (Cu, Pb), as well as for total risk (sum of individual risks). Water column risks are generally lower than sediment risk, except for water column chronic risk for lead that is higher than sediment risk for lead. Acute toxicity is always lower than chronic toxicity. The assumption of constant Acute-To-Chronic toxicity ratio dictates the linearity of the relationship shown in Figure 4.122.12.

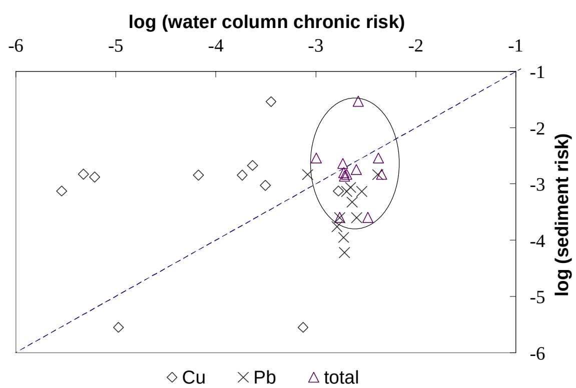

Figure 4.10. Sediment and chronic water column risks.

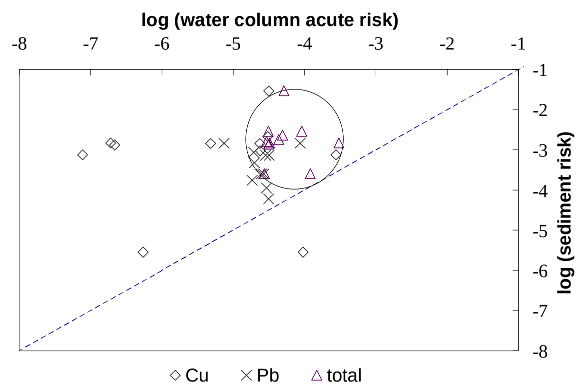

Figure 4.11. Sediment and acute water column risks.

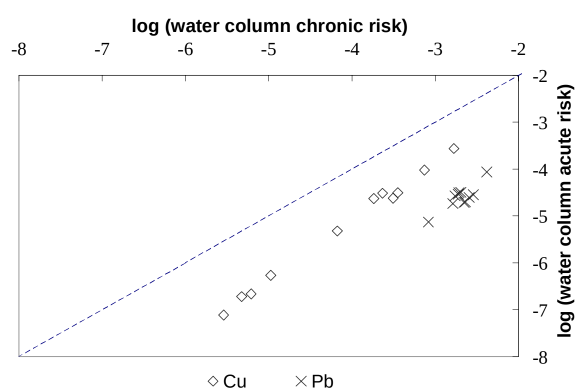

Figure 4.12. Acute and chronic water column risks.

Total water column chronic risk and total sediment risk are close-to-equal while total water column acute risk is significantly lower than total sediment risk (see Figures 4.10 and 4.11, the range of total risks is delineated by an ellipse).

GIS Model

GIS model has been applied to the Oak Creek and Menomonee River watersheds. One of the main advantages of using GIS is presentation of the results. Spatial distribution of sediment loads in the Oak Creek watershed is shown in Figure 4.13. Table 4.14 than shows numeric results of calibrated model. The results are compared to measured loads. Most of the results are within 10% of measured values, with the exception of sediment for the Menomonee River (30%) and copper and lead for the Oak Creek (45% and 20%, respectively).

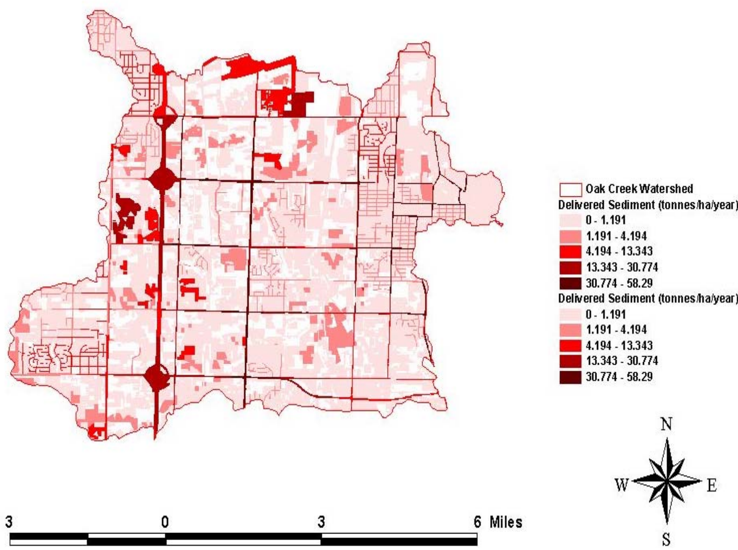

Figure 4.13. Delivered sediment in Oak Creek watershed.

Table 4.14. Comparison of measured and calculated pollutant loads.

Annual load	Menomonee River		Oak Creek	
[tonnes/year]	Measured	Modeled	Measured	Modeled
Sediment	2874	3677	1067	1144
Zinc	1864	1893	521	541
Copper	924	893	146	213
Lead	1211	1247	616	741

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